Assessment of the mechanical behaviour of glass fibre composites with a tough polydicyclopentadiene (PDCPD) matrix

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Abstract

The use of a tough thermoset polydicyclopentadiene (PDCPD) as a matrix material for composites was explored. A PDCPD-glass fibre composite and an equivalent epoxy composite were compared. Fibre-matrix adhesion quality was assessed by transverse bending tests. The materials were subjected to compression tests, impact tests, static tensile tests and tensile fatigue tests. The results indicate that the tough behaviour of the PDCPD matrix markedly influences the composite damage resistance. The size of the impact damage in the PDCPD composite was half of that in the epoxy composite. The tensile tests indicated no significant difference in tensile strength, but the damage before failure was found to be much more severe in the epoxy samples. The fatigue results showed a much lower variation in fatigue life for the PDCPD material than for the epoxy material, as well as clear differences in damage development for the two materials.

Keywords

A. Thermosetting resin; B. Damage tolerance; B. Mechanical properties; polydicyclopentadiene (PDCPD)

1 Introduction

Most of today's composites consist of glass or carbon fibres, combined with a thermoset matrix, mostly epoxies or polyesters. These thermosets are easily available and allow for versatile and efficient composite production processes to be used, like resin transfer moulding or vacuum infusion.

A major disadvantage of epoxies and polyesters, however, is their relative brittleness. Composites using these materials as a matrix are generally also brittle materials, which are sensitive to impact damage and which can fail in an explosive manner, often without much prior warning.

For a number of applications, thermoplastic resins have proven to be valuable alternatives and are frequently used. However, they also possess certain important drawbacks. The main disadvantage is the very high melt viscosity of thermoplastics, making any infusion type of composite production process virtually impossible.

For this reason, numerous attempts, varying in success rate, have been made to improve the toughness of thermosets, or to find new thermosets with enhanced toughness. Toughening of epoxy resins for example can be done by adding rubber particles, thermoplastic particles or other additives. Extensive reviews on rubber-toughening epoxies were made by Bagheri et al. [1] and Ratna and Banthia [2]. Two main methods are used. One is using reactive oligomers that can form a rubber phase by precipitation inside the epoxy matrix. The other involves adding so-called 'core-shell' particles that consist of a rubbery core surrounded by a rigid glassy shell. The latter method is found to give better thermo-mechanical properties [3]. The addition of rubber particles to epoxy resin may increase the fracture toughness, but can also have important drawbacks, the most important being a reduced stiffness and yield strength [4]. The addition of thermoplastic particles instead of rubber particles has the advantage that the reduction in mechanical properties is less pronounced. Thermoplastic toughening is discussed for example by Hodgkin et al. [5] and Pearson et al. [6]. The addition of other nano or micro sized particles such as nanoclay or carbon nanotubes is also considered for epoxy toughening. Zhao and Hoa [7] and Hsieh et al. [8] have investigated the toughening mechanism in and the mechanical properties of nano particle-toughened epoxies.

The effect of using toughened thermosets or thermoplastic matrices on the mechanical properties of composites has been investigated by many researchers e.g. in [9-13]. Fenner and co-workers [10], for example, have analysed the behaviour of a carbon nanotube reinforced epoxy matrix composite. They observed significant improvements in interlaminar shear strength and fracture toughness. Poon

et al. [11] made an assessment of the impact damage in composites produced from different types of toughened epoxies. They noted less pronounced impact damage and significantly higher compression after impact strength. Vieille et al. [12, 13] looked at the impact and post-impact properties of PPS and PEEK based laminates and observed about 50% lower delamination area after impact, compared to epoxy counterparts for an impact energy of 10J. Similar results were obtained by Bishop for a carbon-PEEK laminate compared to a carbon-epoxy laminate [14].

Manjunatha et al. [15, 16] looked at the tensile fatigue behaviour of a silica nanoparticle-modified glass fibre reinforced epoxy composite. These researchers noted improvements of up to 10 times in fatigue life by the addition of silica nanoparticles. Böger observed similar results [17].

Although epoxy is a brittle thermoset, thermosets that possess some inherent toughness do exist. A relatively young thermoset resin with high toughness that seems to be promising for use in composite materials is polydicyclopentadiene (PDCPD) [18]. PDCPD is obtained through ring opening metathesis polymerisation (ROMP) of DCPD monomers upon addition of a metathesis catalyst. Although the ruthenium-based catalyst is expensive, it is highly efficient, so only very low loading is needed to obtain good polymer properties, keeping the cost acceptable. PDCPD shows an interesting combination of properties. Some of the main characteristics of the PDCDP formulation used in this study are listed in Table 1, as well as those of the standard brittle epoxy that is used for reference in this study.

Current areas of applications for PDCPD include large to very large parts often used in harsh environments, for example body panels for agricultural and construction equipment, trucks and buses. In these applications, the high toughness, that is retained at low temperatures, is a major advantage. Several other industries use PDCPD for its chemical resistance (marine applications and in industries like chlor-alkali). Research on polydicyclopentadiene has shown that the good strength and elongation properties are retained at cryogenic temperatures. This makes PDCPD an excellent neat material and polymer matrix for composites in cryogenic applications [10].

PDCPD is an interesting material for use in composites: thanks to the very low viscosity, DCPD formulations offer fast and efficient fibre wetting within a short time period. Thanks to the tuneable nature of the metathesis catalysts, DCPD is suitable for very fast processing (fast RTM) or for showing extended working life at room temperature, with thermal triggering on demand. Typical cycle times for DCPD RIM are around 5 minutes. In contrast, epoxy resins showing an improved toughness are typically by far more viscous and difficult to process.

Also, the chemical nature of PDCPD makes it resistant towards hot, wet and corrosive environments. Literature data demonstrates that PDCPD/fiberglass composites exhibit exceptional resistance to hot wet environments, superior to epoxy/fiberglass composites tested in the same conditions [19]. These characteristics make PDCPD composites better-suited to applications in harsh environments, such as wind energy structures, offshore oil platforms, and both land and marine.

Very limited results have been published looking into the mechanical properties of composites with PDCPD matrix. In the framework of the SNL/MSU/DOE project on wind turbine blade materials, however, an extensive experimental program including also some tests on this type of materials has been carried out [20-22]. These researchers compared the mechanical properties of PDCPD-glass laminates to that of epoxy-glass counterparts. Note that the PDCPD used in the mentioned study was a particular formulation called Proxima™, produced by Materia, Inc. There is not a lot of information available on this type of material. It is based on DCPD and it is claimed that this formulation shows favourable toughness, viscosity, and chemical resistance compared to traditional PDCPD formulations. Giardello et al [23] (Materia Inc) described the use of adhesion agents that can be incorporated into cyclo-olefin based formulations to make them compatible with an existing, commercial coating or treatment. For example, for use with an amino-silane treated glass substrate, olefin compounds containing isocyanate functional groups are particularly good adhesion agents. It seems reasonable to assume that the Proxima™ resin contains other monomers improving the solubility of glass fibre sizing ingredients and the interfacial adhesion to commercial glass fibres. On the other hand, the Proxima™ resin seems to have a low glass transition temperature of only 124 °C

[19]. The typical T_g value for pure DCPD transformed by RIM process is 155°C (by DSC) and the T_g of the F2.06 PDCPD formulation reported in this article is 215°C.

The researchers reported similar in-plane mechanical properties for the two materials, and found a G_{Ic} value for the PDCPD composite of 1729 J/m². The G_{IC} initiation value found for the composite with the PDCPD formulation used in the present study (1065 J/m², see table 2), is considerably lower, but still in the range typically observed for composites with highly toughened epoxies or high-performance thermoplastics as illustrated in Table 2. The tensile fatigue performance observed in [20-22] was similar to that of the epoxy resin composites, while a slightly improved compressive fatigue resistance was observed for the PDCPD laminates. Tests on a complex structured coupon with two ply drops revealed an increase of about 30 % in the static load required to produce large-scale delamination in the PDCPD composite, as well as higher reversed loading fatigue cycles to obtain the same damage length in the complex coupon [22].

The present paper contains the results of an exploratory study, analysing several aspects of the mechanical performance and damage behaviour of glass fibre reinforced composites with a special high T_g PDCPD grade (T_g = 215°C) for the matrix, as compared to an equivalent (brittle) epoxy composite.

2 Materials and test methods

2.1 Materials and production

The matrix materials used for this study were a specialty DCPD based formulation (type F2.06) with high T_g, and a standard epoxy resin (Epikote 828 LVEL with Dytek DCH 99 hardener [24]). The epikote epoxy resin was selected because it is a very standard, non-toughened epoxy with a rather low viscosity. Benchmarking against such a standard material in this initial stage of research will make clear if there is any added value in the use of PDCPD in composites.

The glass fibres for this study were supplied by PPG Fiberglass. Two types of E-glass fibres were used: For the epoxy composites, PPG 1383 was used. Typical glass sizing formulations used in commercial glass fibres are compatible with polar epoxy matrices. They are incompatible with the non-polar

F2.06 formulation as the sizing layer forms a barrier between the matrix and the glass surface. Therefore, a special type of fibre, T73, was used. This contains a proprietary sizing that consists of organosilane and other ingredients necessary for the fibre processing. This sizing is compatible with DCPD monomers, and enables efficient fibre/matrix bonding. Both types of glass were available as rovings (direct draw) and as a plain woven fabric with an areal density of 800 g/m².

Two types of composites were produced with the above materials: unidirectional samples and woven fabric laminates. Production of the composites was done by Telene SAS.

Unidirectional (UD) samples were produced by means of a 'hand pultrusion' process: fibre bundles are impregnated with the uncured resin, pulled through a mould, and subsequently cured. For the compression test samples, the mould was a rectangular glass tube with an inner cross section of approximately 8 x 4 mm². For the transverse three point bending tests, wider and thinner plates were needed to make transverse samples, so a mould with a cross-section of 2 x 70mm² was used. Because of the higher viscosity of the epoxy matrix material, it was impossible to use the same amount of fibres in this case as for the PDCPD composites. This resulted in a 5% lower fibre volume fraction for the epoxy composite.

Woven fabric laminates were produced by vacuum infusion of 4 layers of glass fibre weave with the F2.06 PDCPD and the epoxy.

The process parameters (and the resulting T_g of the materials) for the infusion and pultrusion process are listed in Table 3.

2.2 Test methods

2.2.1 Quality control, fibre volume fraction measurements

Because of the non-standard production method, a few samples produced by hand-pultrusion were investigated by nano-CT (Phoenix NanoTom S (GE Measurement and Control Solutions, Wunstorf, Germany) to assess the general sample quality. A voxel size of 6.25 µm was used. Fibre orientation and composite porosity were evaluated qualitatively, based on the X-ray images.

Composite fibre volume fractions were measured by means of the resin burn-off technique (ASTM 3171). The density values used for the calculations were 1.03 g/cm³ for the PDCPD, 1.16 g/cm³ for the epoxy and 2.54 g/cm³ for the glass fibres.

2.2.2 Adhesion assessment by three point bending

Transverse three point bending (3pb) tests were done to provide an indication of the quality of the bond between fibres and matrix. The technical details for the bending tests can be found in Table 4. The test samples were cut from wide unidirectional rods by means of a water-cooled diamond saw. The edges were sanded to eliminate damage resulting from the cutting. The fibre direction in the samples was perpendicular to the length axis. A span length of 40 mm was used.

2.2.3 Compression tests

Compression tests were done on the hand-pultruded unidirectional samples of the T73-PDCPD F2.06 and PPG 1383-epoxy combinations. Sample dimensions and other technical details of the tests are again in Table 4. 1.5 mm thick aluminium end tabs were glued to the ends of the samples, leaving a gauge length of 15 mm. Strain measurements on the front and back side of the samples were done by digital image correlation (Limess Snapshot system). The strain was measured over a length of approximately 8 mm.

2.2.4 Static and fatigue tensile tests

Table 4 lists the technical details of the static and fatigue tests. As for the compression tests, strain measurements during the static tests were done by means of digital image correlation over a sample length of approximately 25 mm.

Fatigue tests were done in load-controlled mode on a 160 kN hydraulic Schenck. The ratio between the minimum and maximum applied fatigue load (R-ratio) was 0.1. The sample temperature was regularly monitored during the test to avoid excessive heating of the samples. The maximum temperature increase measured was 15 °C, which occurred only during the final stages of the test, when there was a rapid build-up of damage. As an indication of the stiffness evolution during fatigue,

the chord modulus was determined as the ratio of the difference in load over the difference in displacement for each cycle.

2.2.5 Drop weight impact tests

Drop weight impact tests were done on 100x100 mm² samples cut from the woven laminates. A semi-hemispherical impactor with a diameter of 16 mm was used for the tests. The impactor weight was 3.120 kg, and the drop height was either 490 mm or 815 mm, which resulted in a potential impact energy of 15 or 25 joules. Assessment of the impact damage was done by means of visual inspection with the aid of transmitted light, as well as by ultrasonic C-scan.

3 Results and discussion

3.1 Quality control

An example of a longitudinal and transverse tomography slice of a hand-pultruded sample is shown in Figure 1. As can be seen on the right-hand image in the figure, the fibre distribution in the samples is not uniform. This is the result of the way the samples are produced (pulling several impregnated rovings through a mould). This means that there will be some local fibre volume fraction variations in these samples. No clear evidence of defects or voids was found in these samples, and no significant fibre misalignment was observed. Therefore, the overall quality of the samples was judged acceptable and sufficient for the tests.

Because of the transparent nature of the PDCPD and epoxy glass composites, the quality of the woven fabric infused laminates could be judged by visual inspection. No evidence of significant fibre misalignment or porosity was observed.

The overall quality of the epoxy-glass laminates used for the tests was acceptable. Relatively high variations in thickness measurements were sometimes observed when preparing the mechanical tests. The variation in thickness over the whole laminate amounted to a maximum of about 10%, but inside individual samples the variations were much smaller (maximum about 5 %). Per sample, several thickness measurements were done and the average was used in the calculation of stresses.

No influence of the thickness variations was found on the location of damage or final failure (which was not localised for the epoxy laminates). The DIC strain fields also did not show non-uniform strains during the tests. This is understandable, because all these tests were done in fibre direction, and the absolute fibre content was the same for all samples.

For the PDCPD laminates, the overall quality was also judged acceptable, although these laminates showed limited amounts of 'white streaks' parallel to the local fibre direction. These are believed to be caused by matrix shrinkage during production. These pre-existing defects in the PDCPD composites were not found to be initiation sites for further damage during the tests.

The measured glass fibre volume fractions for the different types of samples are shown in Table 5. As predicted, the fibre volume fraction of the epoxy compression samples was slightly lower (8 % relative difference) than that of the PDCPD samples. For the transverse three point bending samples, the difference was a bit smaller (about 5 % relative difference). For the laminates, the fibre volume fraction of the epoxy laminates was about 5 % (relative difference) higher than that of the PDCPD laminates.

3.2 Adhesion assessment with three point bending test

To investigate the quality of the fibre-matrix adhesion of the PDCPD F2.06 /T73 glass combination, a series of transverse three point bending tests was done on unidirectional samples. The results were compared to the epoxy/PPG 1383 glass combination, which is known to have sufficient adhesion. The tests were also done on samples of PDCPD F2.06 combined with the epoxy-compatible PPG 1383 fibres. This combination was expected to be of poor quality because of the combination of a polar sizing with the non-polar PDCPD. Visual inspection of the latter samples indeed suggested that they were of poor quality: bad impregnation (dry fibres on the surface) and lack of transparency were observed. These samples were nonetheless still tested for the sake of completeness.

It should be noted that the obtained three point bending strengths of the PDCPD F2.06 /T73 glass and the epoxy/PPG 1383 glass combination do not represent the actual fibre-matrix adhesion strength. Failure of this type of test may be located in the interface between fibre and matrix, in the

matrix, or a combination of both. However, if failure is in the interface, a rather weak adhesion can be assumed, giving rise to low observed bending strengths. The main purpose of this test series was to check if the adhesion quality of the PDCPD matrix to the T73 fibres was sufficient and at least comparable to that of the epoxy/glass combination.

Table 6 shows the average obtained transverse three-point bending strength for the three materials.

The obtained strength for the PDCPD F2.06 /T73 combination was significantly higher (p-value of 0.002) than that for the EP/PPG 1383 combination. Since the EP/ PPG 1383 combination is known to have good adhesion, adhesion between fibres and matrix in the PDCPD F2.06 /T73 material can therefore also be considered very good.

Since the fibre volume fraction of the epoxy samples was about 5 % lower than that of the PDCPD F2.06 /T73 composites (see Table 5), it can be expected that the difference between the two would become slightly larger if the two materials had the same fibre volume fraction. Since this is a transverse test, an increase in the fibre volume fraction in the epoxy composite can decrease the inter-fibre spacing and lead to a decrease in observed transverse tensile strength. The PDCPD F2.06/PPG 1383 combination results in very low values, due to the bad impregnation. Hence it cannot be directly compared to the other two results. It can, however be concluded that there is little compatibility between the PDCPD and the PPG 1383 glass.

3.3 Compression

During the compression tests, no excessive global buckling was noted in any of the tested samples, in accordance with the procedure outlined in the relevant testing standard. Table 7 shows the obtained compressive strength and compressive modulus for both types of samples, as well as the values normalised to a fibre volume fraction of 50 %. The results indicate that the modulus for the PDCPD samples is significantly higher (19 %, p-value=$2x10^{-5}$) than that of the epoxy samples. After normalisation, however, the difference decreases to about 9 %, and the p-value becomes 0.002.

The compression strength of the two materials as-measured does not differ significantly (p=0.45). After normalisation, however, the strength of the PDCPD composite is about 11 % lower than that of

the epoxy composite, with a p-value of 0.03. This difference is likely related to the lower stiffness of the neat PDCPD compared to epoxy (1.9 GPa vs. 3.0 GPa). Note that concerning the compressive strength of composites, the influence of the fibre volume fraction is not straight-forward, and therefore the linear normalisation used here is not entirely valid.

3.4 Tensile tests

The results from the tensile tests on the woven fabric composite samples are shown in Table 8. Final failure was in the gauge section for all tested samples. No significant difference between the two materials was measured in terms of stiffness, even after normalising the results to a fibre volume fraction of 50 % (p=0.08). This is not surprising, since the stiffness is mainly fibre dominated. The strength as-measured also showed no difference (p=0.34). However, after normalisation, the strength of the PDCPD laminate was found to be about 9 % higher than that of the epoxy composite, with a p-value of 0.03. The failure strain for the epoxy samples was found to be marginally larger than that of the PDCPD composite. This may be explained by the pronounced loss in stiffness of the epoxy samples near the end of the test, caused by the build-up of extensive delamination damage.

The pictures taken during the test with transmitted light reveal a markedly different damage development, which is also reflected in the shape of the tensile curves. Figure 2 shows transmitted light pictures taken during the tensile tests for different percentages of strain for both materials. Tensile curves for the two materials are shown in Figure 3.

The PDCPD composite does not show damage up to around 1 % of strain (except for the production related artefacts mentioned in section 3.1), after which a very limited amount of short, localized transverse and longitudinal cracks start to develop. This is accompanied by a very slight and gradual decrease in slope of the tensile curve. The first signs of the onset of delamination are in the second to last picture. This was taken approximately 1 second before failure (called JBF in the figure), i.e. at a strain virtually equal to the failure strain. Final failure is very localized and consists of fibre failure with a very limited amount of delamination. In the epoxy composites, however, after 0.5 % of strain a multitude of transverse matrix cracks can already be seen. Not only are they more numerous, they

are also longer and were seen to grow very quickly over the full width of the sample. This is reflected in the tensile curve by a marked decrease in the slope of the curve of up to 30 %. The number of transverse cracks increases rapidly with increasing strain. Between 1 and 2 % of strain, also longitudinal cracks are found to develop. The first delaminations occur between 2 and 2.5 % of strain and are localized on the 'cross-over' points of the fibre bundles (as may be expected in a woven fabric laminate). Many delaminations are formed, which grow and coalesce and finally cause failure by extensive delamination and fibre failure. The growth of delaminations in the epoxy laminate again has a pronounced influence on the slope of the tensile curve, which is found to decrease further. For the PDCPD laminate, however, the slope remains more or less constant up to failure. The observed delay in damage development in the PDCPD laminate may explain the slightly higher normalised tensile strength.

The difference in behaviour between the two materials is remarkable and is an indication that the tough behaviour of the pure PDCPD material is retained when used as a matrix material in composites. The toughness leads to a better resistance to the formation and growth of matrix cracks and delaminations than more traditional (brittle) thermosets.

3.5 Tensile fatigue

Tensile fatigue tests were run at load levels of 250, 200 and 150 MPa. Since the tensile strength of both materials was approximately 500 MPa, this corresponds to 50, 40 and 30 % of the tensile strength. The fatigue life data are shown on the graph of Figure 4. It should be noted that, as opposed to the static tests, a relatively high percentage (about 65 %) of fatigue samples did not fail in the gauge area, but rather close to or in the end tabs. There was, however, no clear difference in fatigue life between samples that failed at the tabs and samples that did not.

Two observations were made when analysing the obtained fatigue life data:

- The fatigue life data for the PDCPD composite clearly seem to be situated in the higher end of the range of the epoxy composite results, although strictly speaking the difference in average fatigue life is statistically not significant for an α-level of 5 % ($p=0.06$). The

improvement in average fatigue life that is suggested from the present results is of the same order as that which was found for composites with nanoparticle-toughened epoxy matrices [15-17].

- For all tested load levels, the variation in fatigue life for the PDCPD composite is much smaller than that for the epoxy composite. For a certain fatigue load level, the difference between the lowest and highest observed fatigue life is about a factor ten for the epoxy composite (i.e. one order of magnitude, which is in line with what is commonly observed for epoxy composites), while for the PDCPD laminate this difference is less than a factor three.

Because of these observations, for both materials the 95 % confidence interval was determined in accordance with the ASTM E739 procedure, as outlined by Sutherland and Veers [25]. The methodology is based on two assumptions: (1) the relationship between the log of the measured life (N cycles) is a linear function of the stress or the log of the stress, and (2) the distribution function of the residuals about the mean line is homogeneous; i.e., it does not depend on the stress level. The 95 % interval is also indicated on Figure 4. The bottom dashed line of these intervals indicates the lower limit of the region containing, with 95 % confidence, 95 % of all future fatigue test results for this material. Examination of these curves shows a very clear difference between the two materials, as suggested already by the above observations. This so-called 95/95 fatigue life is clearly much higher for the PDCPD composite than for the epoxy composite. The latter is a valuable result, because this 95/95 fatigue life curve is often used when designing composite structures for fatigue sensitive applications. The high scatter that is commonly observed in fatigue data (around one order of magnitude is no exception) causes the 95/95 fatigue life to be rather low, like in the present case for the epoxy composites, and therefore gives rise to very conservative designs. The graph in Figure 5 shows the evolution of the chord modulus during fatigue at 150 MPa (30 % of the tensile strength). The chord modulus is the ratio of (maximum load-minimum load)/(maximum displacement-minimum displacement) for each cycle. The evolution of this modulus may be seen as representative for the

evolution in the stiffness of the sample during fatigue. The graph indicates that the reduction in modulus for the epoxy samples is more pronounced than for the PDCPD samples.

The above observation is supported by the evolution of damage in this type of samples during tensile fatigue as shown in Figure 6. The somewhat lower quality of the PDCPD laminate and the alleged shrinking cracks, mentioned in section 3.1, can be seen in the PDCPD material prior to loading. After 100 cycles, clear transverse cracks can already be seen in the epoxy composite. At this moment, only a very limited amount of short, localised cracks is found in the PDCPD composite. As the number of cycles increases, short longitudinal cracks are also created. After around 1000 cycles, the onset of local delamination from the cracks is observed for the epoxy composite, while in the PDCPD composite there is no sign of delaminations at that time. At 10 000 cycles, starting delaminations are also observed in the PDCPD composite. As the number of cycles increases, extensive areas of delaminations are formed in the epoxy composite, while the progression of this type of damage is much slower in the PDCPD composite. This explains the smaller decrease in the chord modulus observed for the latter material. The overall damage evolution in the two materials is in general very similar to that during a static tensile test, although the degree of (localised) delamination in the PDCPD composite during fatigue seems to be slightly higher than during static testing.

3.6 Drop weight impact damage

From speed measurements just before and after the impact, the kinetic energy was determined. The difference between the kinetic energy just before and after the impact equals the absorbed energy. This energy is used during the impact, e.g. for the formation of damage and/or for plastic deformation of the sample. The absorbed energy per mm thickness of the sample for these impact tests is shown in the graph in Figure 7.

Thanks to the transparent nature of the samples, visual inspection of the impact damage was possible. An example of a transmitted light photograph for both the DPCPD and the epoxy specimens, impacted with an energy of 25 J is shown in Figure 8. For both the 15 and 25 J energy levels, such inspection clearly showed that the damage in the epoxy laminates is more severe than

that in the PDCPD laminates. A central delaminated region with a very limited amount of fibre damage is visible on the impact site. In the epoxy samples this region is surrounded by matrix cracks. These are not distinguishable in the PDCPD laminate, although a slightly more opaque region around the delaminated area suggests the presence of either micro-cracks or fibre/matrix debonding.

C-scan ultrasonic imaging was used to determine the size of the delaminations in the impacted samples. This is a transmission type of scan. Therefore, the result of the scan is not the sum of all delamination surfaces present in the material, but rather the projected surface of all superposed delaminations. The results of the scans for both impact energy levels of the two materials are shown in Figure 9.

All the obtained data from the impact tests indicate a significant difference in delamination size between the PDCPD and the epoxy laminates for equal impact energy ($p=0.001$ for 15J/mm impact energy, and $p=0.0001$ for 25J/mm impact energy). For both impact energy levels tested, the measured delamination size is found to be more than two times larger for the epoxy laminate than for the PDCPD laminate. These results are similar to the improvement seen for PEEK matrix composites compared to epoxy laminates [12-14], and for toughened epoxy laminates [11], as mentioned in the introduction. The findings again clearly indicate a tougher behaviour of the PDCPD composite. The reduced level of impact damage in these samples can be expected to lead to improved post-impact performance (e.g. compression after impact).

4 Conclusions

The present study was aimed at making an assessment of a number of basic mechanical properties of glass fibre composites produced with PDCPD, compared to those of a basic epoxy laminate. The main goal was to investigate if the high toughness of the PDCPD resin would lead to significant differences in the laminate behaviour.

For the PDCPD composites, a high T_g F2.06 PDCPD matrix was used in comparison to the reference epoxy composites. The F2.06 PDCPD requires a high post-cure temperature (190°C) which results in a glass transition temperature of around 215°C. The epoxy/glass composites were post cured at 150°C

and showed a T_g of 155°C. Due to the non-polar nature of the PDCPD matrix, a special glass sizing is required to achieve a good fibre/matrix adhesion. Typical commercial glass fibres with epoxy type sizing are not compatible with the DCPD based formulation and form a barrier between the glass and the PDCPD, preventing access to the glass surface. The epoxy composites were prepared by using commercial PPG 1383 glass.

Fibre-matrix adhesion, compressive properties, static and dynamic tensile behaviour and drop-weight impact behaviour were investigated. The adhesion between the T73 glass fibres and the PDCPD F2.06 matrix was found to be at least equal to that of the standard PPG 1383 fibres/Epikote resin combination. A slightly higher (normalised) compressive modulus was noted for the PDCPD composite. The compressive strength after normalisation was lower than for the epoxy composite, probably due to the lower matrix stiffness.

No significant difference was found in the tensile stiffness and strength as-measured, but after normalisation, the tensile strength of the PDCPD composite was about 9 % higher than that of the epoxy composite. Transmitted light pictures taken during the tensile tests revealed a much less pronounced development of damage in the PDCPD laminate: matrix cracks appeared later, and were less numerous than in the epoxy laminate. Moreover, the degree of delamination developed near the end of the test was found to be reduced greatly.

A similar difference in damage development was noted during tensile fatigue loading. The fatigue life data of the PDCPD samples were situated in the higher region of the scatter band of the epoxy samples data, and the scatter on the PDCPD data was markedly lower. This led to a marked difference in 95/95 fatigue life.

Also in the drop-weight impact tests, the PDCPD composite showed a tougher behaviour: the size of the projected delamination area was found to be less than half of that measured in its epoxy counterpart for both of the impact levels tested.

The observations made in this study show that the toughness of the neat PDCPD indeed leads to a tougher composite, if there is sufficient adhesion between fibres and PDCPD. The observed

behaviour is very similar to that of PEEK or toughened thermoset composites. PDCPD is therefore a promising matrix material for use in composite materials, especially in areas where toughness and impact resistance are key issues. Further research into the mechanical behaviour of these composites is necessary, however, to fully characterise and verify the behaviour. In-depth analysis of the interlaminar toughness behaviour can provide information that can help to explain for example the damage development and impact behaviour. Compression after impact tests can show how pre-existing damage will evolve under loading, as will the determination of post-fatigue residual properties.

5 Acknowledgements

This study was financed by the company Telene SAS, which also produced and provided the materials used in the experiments.

Parts of the results in the paper have been preliminary presented in the ICCM-20 conference, 19-24 July 2015, Copenhagen, Denmark [33].

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FIGURE CAPTIONS:

Figure 1: Virtual cross-section images (slices) made by x-ray tomography of unidirectional PDCPD/glass fibre samples produced by hand pultrusion. Left: longitudinal section; Right: transverse section. The width of the samples in both pictures is 3.8 mm. The voxel size for the images was 6.25 µm.
Figure 2: Transmitted light pictures of a PDCPD composite sample (left) and an epoxy composite sample (right) during tensile testing, for various strain levels. JBF indicates just before failure (i.e. one second). Failure was at 2.6 % strain for the PDCPD composite and at 2.7% strain for the epoxy composite. (The direction of the tensile load is horizontal).
Figure 3: Tensile curves of a PDCPD woven composite sample (a) and an epoxy woven composite sample (b). The arrows indicate the knee points in the curve, associated with the development of damage.
Figure 4: The fatigue life data and the bounds of the 95/95 interval for the two materials.
Figure 5: Evolution of the chord modulus of woven fabric composite samples tested in fatigue up to 150 MPa.
Figure 6: Transmitted light pictures at certain numbers of cycles in fatigue tests up to 150 MPa, illustrating the fatigue damage evolution for the epoxy laminate sample (left) which failed at 40567 cycles, and the PDCPD composite sample (right) which failed at 200 107 cycles. (The loading direction in these pictures is horizontal).
Figure 7: Absorbed energy per mm thickness for the two woven laminate materials, for an impact energy of 15 and 25 J.
Figure 8: Transmitted light photograph of an epoxy laminate sample (left) and a PDCPD laminate sample (right), both impacted with an energy of 25 J. The scale for both pictures is the same.
Figure 9: The projected delamination size for both materials and impact energies, as measured by ultrasonic c-scan.

Table 1: Physical, thermal and mechanical properties for the matrices studied in this work.

	PDCPD F2.06	Epikote 828 LVEL + DCH-99
Density (kg/dm³)	1.03	1.16
Modulus (GPa)	1.9	3 [26]
Initial viscosity @25°C (Pas)	< 0.01	10-12 [24]
Tensile Strength (MPa)	60	75 [26]
Elongation at break (%)	*At yield: 5*	4 [26]
Glass transition temperature (°C) (DMA)	215	155

Table 2: Mode I interlaminar toughness data for the composites in this study. For comparison, literature values for another PDCPD composite, toughened epoxy composites and PEEK composites are also given.

	G_{IC} (initiation) (J/m²)	source
PDCPD (Telene F2.06) / glass fibre	1065	Experiment*
Epikote 828 LVEL / glass fibre	319	Experiment*
PDCPD (Proxima™ Materia) / glass fibre	1729	[20-22]
Toughened epoxy composites	700-1700	[27-30]
PEEK composites	1100-1800	[31, 32]

**GIc initiation values obtained according to ISO 15024, using the 5% offset method.*

Table 3: Processing parameters for the two materials and the resulting T_g of the matrix

Matrix type	Impregnation	Cure	Post-cure	T_g*
F2.06 PDCPD	Room temperature	1h@120°C	1h@190°C	215°C
Epikote	40°C	1h@70°C	1h@150°C	155°C

T_g by DMA from tan delta

Table 4: Technical details for some of the performed tests

Test	Standard	Minimum number of samples/material type	Test speed	Nominal sample dimensions (mm^3)
Three point bending tests	ISO 14125	8	1 mm/min	70x10x2
Compression tests	ASTM 3410	6	1.5 mm/min	125x8x4
Static tensile tests	ASTM 3039	5	2 mm/min	250x25x2.3
Fatigue tests	ASTM 3479	15	5 Hz	250x25x2.3

Table 5: measured fibre volume fractions for the different material combinations and sample types. The prefix 'UD' indicates the unidirectional samples produced by pultrusion.

	PDCPD F2.06 – T73	PDCPD F2.06 – PPG 1383	Epoxy – PPG 1383
UD-Compression samples	0.50 ± 0.02	/	0.46 ± 0.05
UD-Transverse 3pb samples	0.59 ± 0.05	0.61 ± 0.05	0.56 ± 0.08
Woven laminates	0.53 ± 0.06	/	0.56 ± 0.06

Table 6: the average obtained transverse three point bending strength and standard deviations. 'UD' indicates that these materials are the 'hand-pultruded' unidirectional composites)

Material	Matrix	Glass fibre type	Three point bending strength (MPa)
UD-PDCPD F2.06/T73	PDCPD F2.06	T73 (PDCPD compatible)	102 ± 14
UD-PDCPD F2.06/PPG 1383	PDCPD F2.06	PPG 1383 (epoxy compatible)	19 ± 7
UD-EP/PPG 1383	Epikote 828 LVEL	PPG 1383 (epoxy compatible)	81 ± 7

Table 7: The compressive strength and modulus. The normalised values (for 50 % fibre volume fraction) are also given. The prefix 'UD' indicates the unidirectional samples produced by pultrusion.

	UD-PDCPD F2.06/T73	UD-Epoxy/PPG 1383
Compressive strength (MPa)	807 ± 45	837 ± 82
Compressive modulus (GPa)	40 ± 1	34 ± 1
Normalised strength (MPa)	807 ± 45	910 ± 89
Normalised modulus (GPa)	40 ± 1	37 ± 1

Table 8: The tensile strength, modulus and failure strain for the two types of woven fabric laminates, and the normalised values (fibre volume fraction = 50 %).

Material	PDCPD laminate	Epoxy laminate
Tensile strength (MPa)	516 ± 14	502 ± 33
Tensile modulus (GPa)	23 ± 2	26 ± 3
Normalised modulus (GPa)	22 ± 2	25 ± 3
Normalised strength (MPa)	487± 13	448 ± 29
Failure strain (%)	2.7 ± 0.1	2.9 ± 0.1

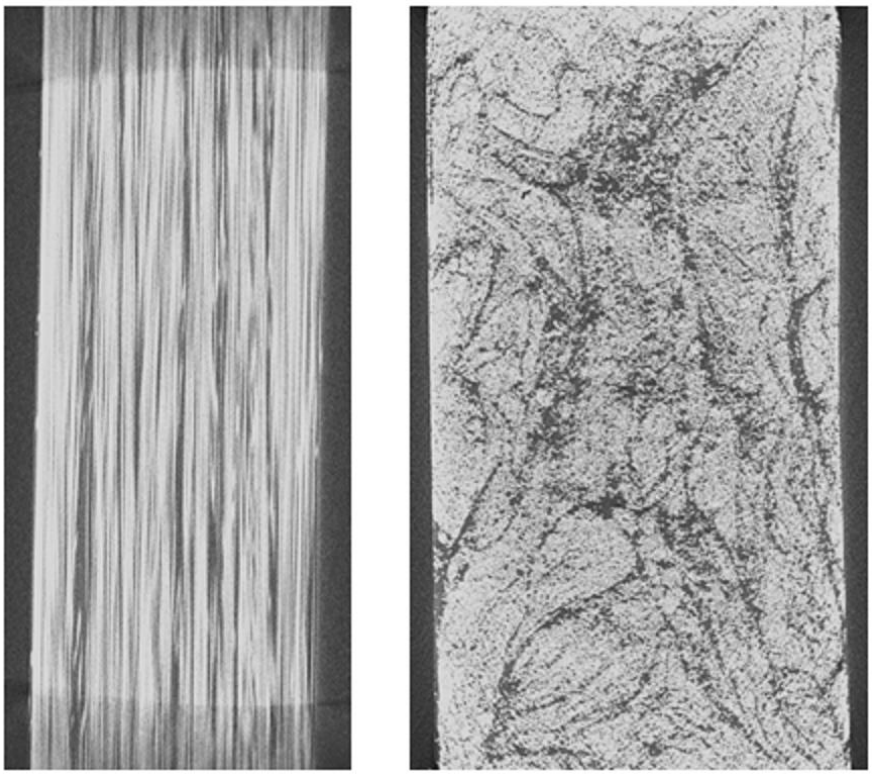


Figure 10: Virtual cross-section images (slices) made by x-ray tomography of unidirectional PDCPD/glass fibre samples produced by hand pultrusion. Left: longitudinal section; Right: transverse section. The width of the samples in both pictures is 3.8 mm. The voxel size for the images was 6.25 µm.

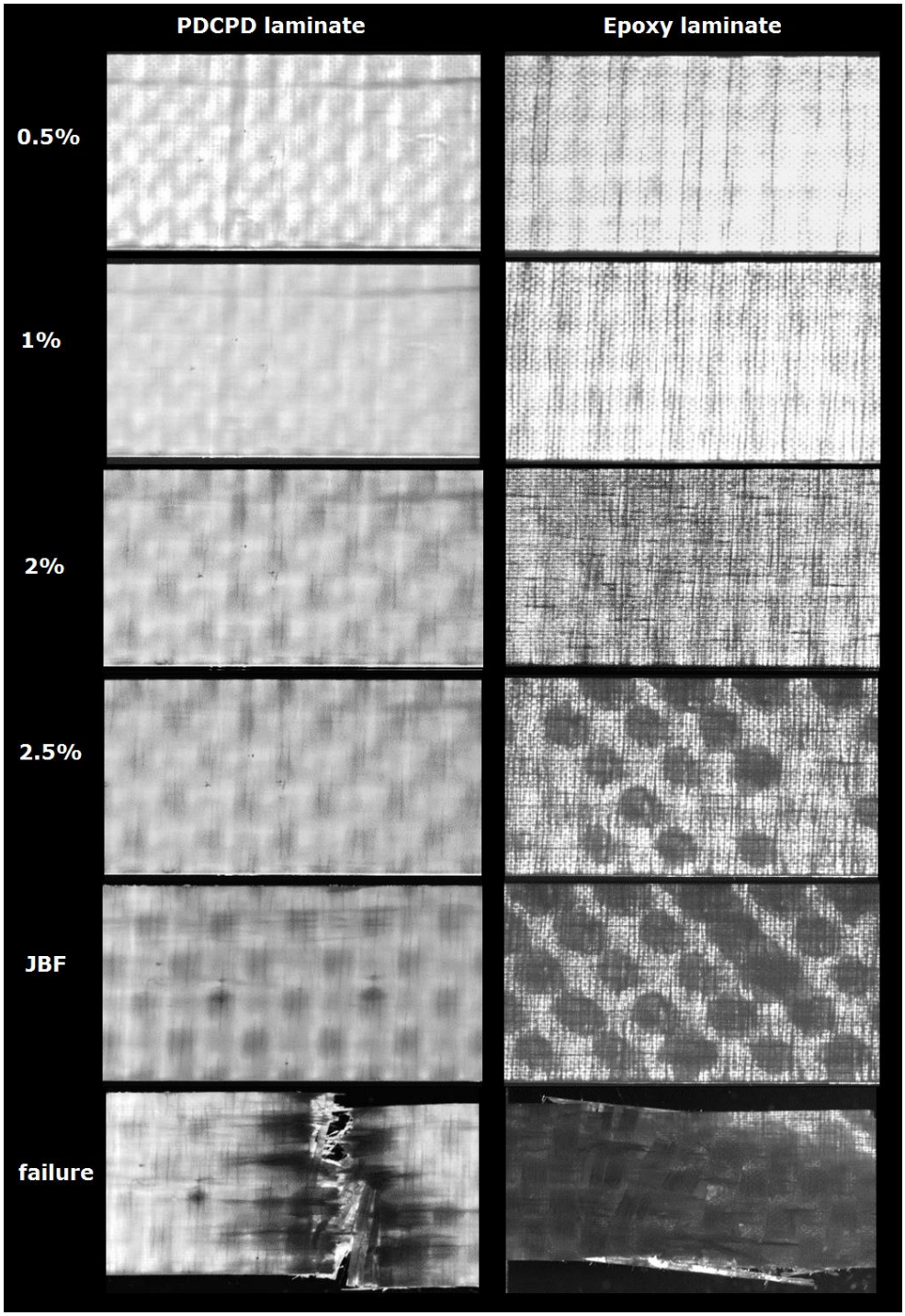
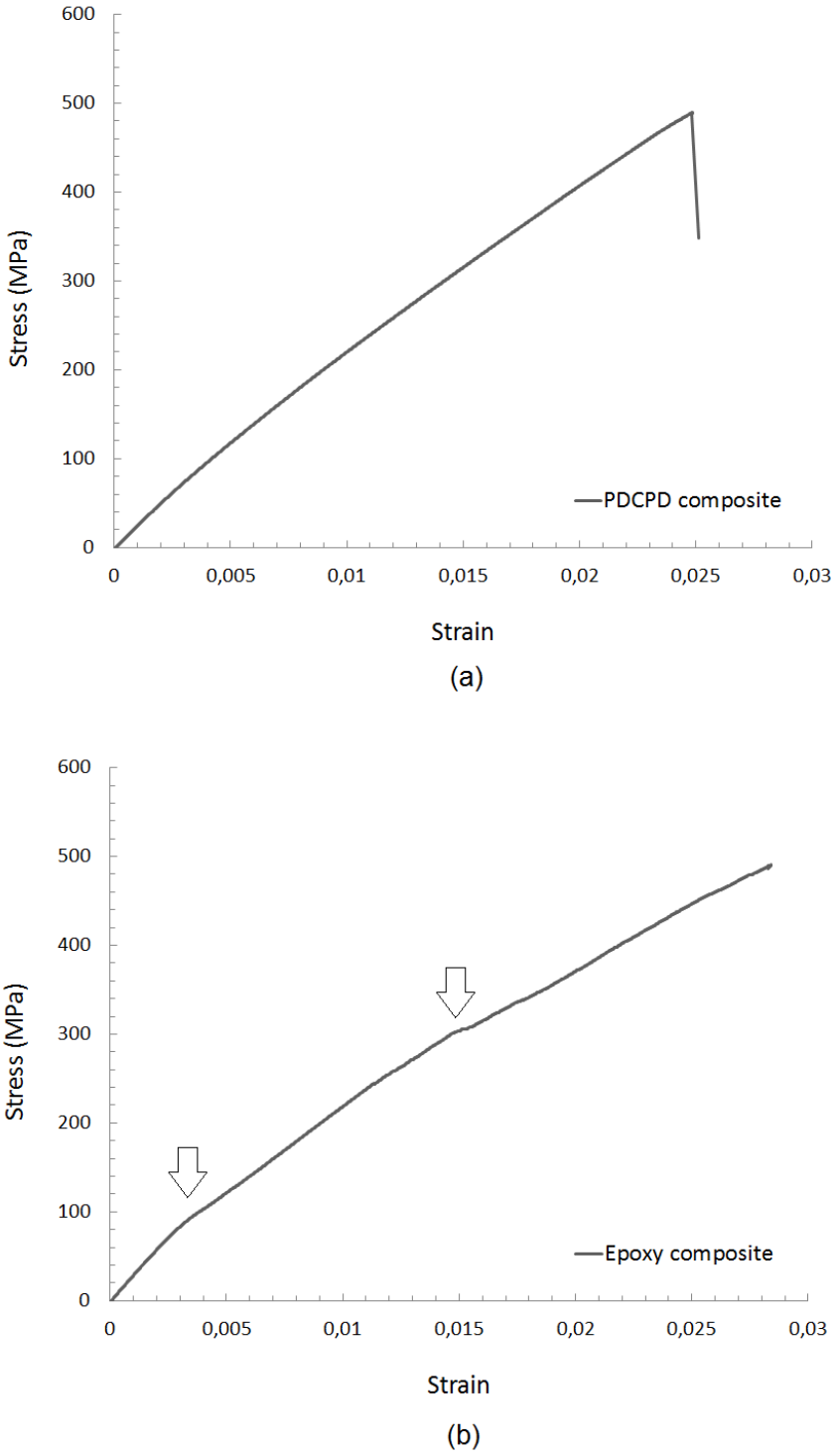


Figure 11: Transmitted light pictures of a PDCPD composite sample (left) and an epoxy composite sample (right) during tensile testing, for various strain levels. JBF indicates just before failure (i.e. one second). Failure was at 2.6 % strain for the PDCPD composite, and at 2.7% strain for the epoxy composite. (the direction of the tensile load is horizontal).



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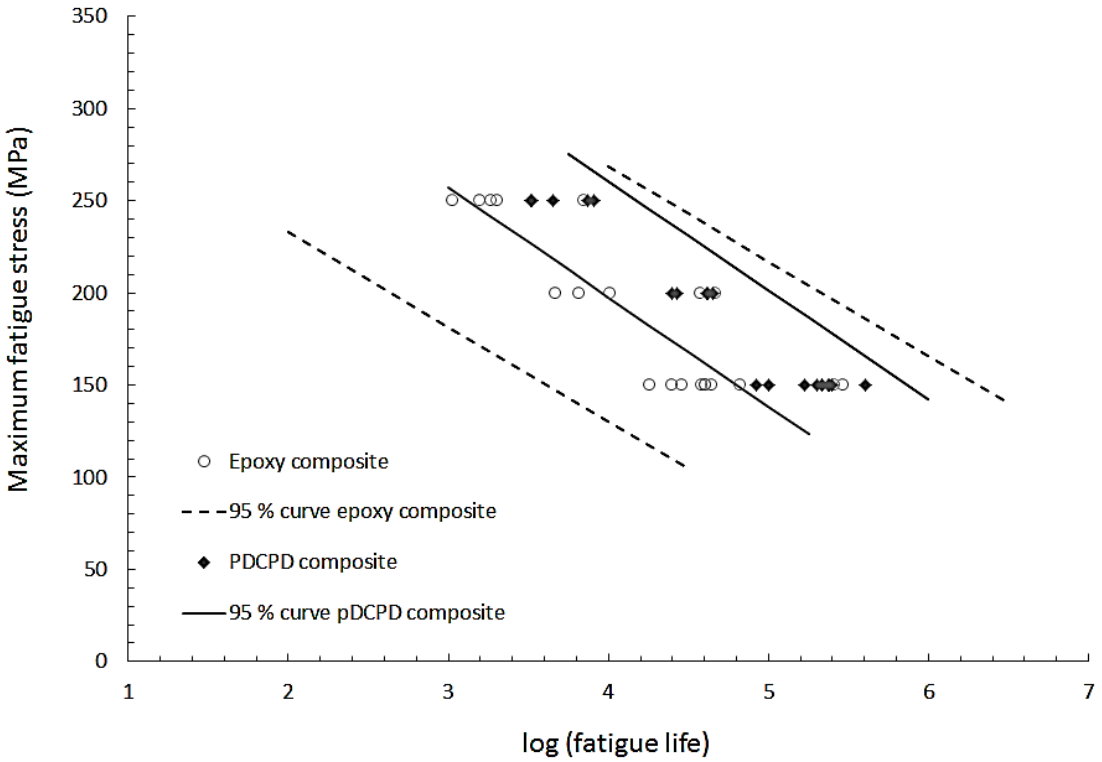

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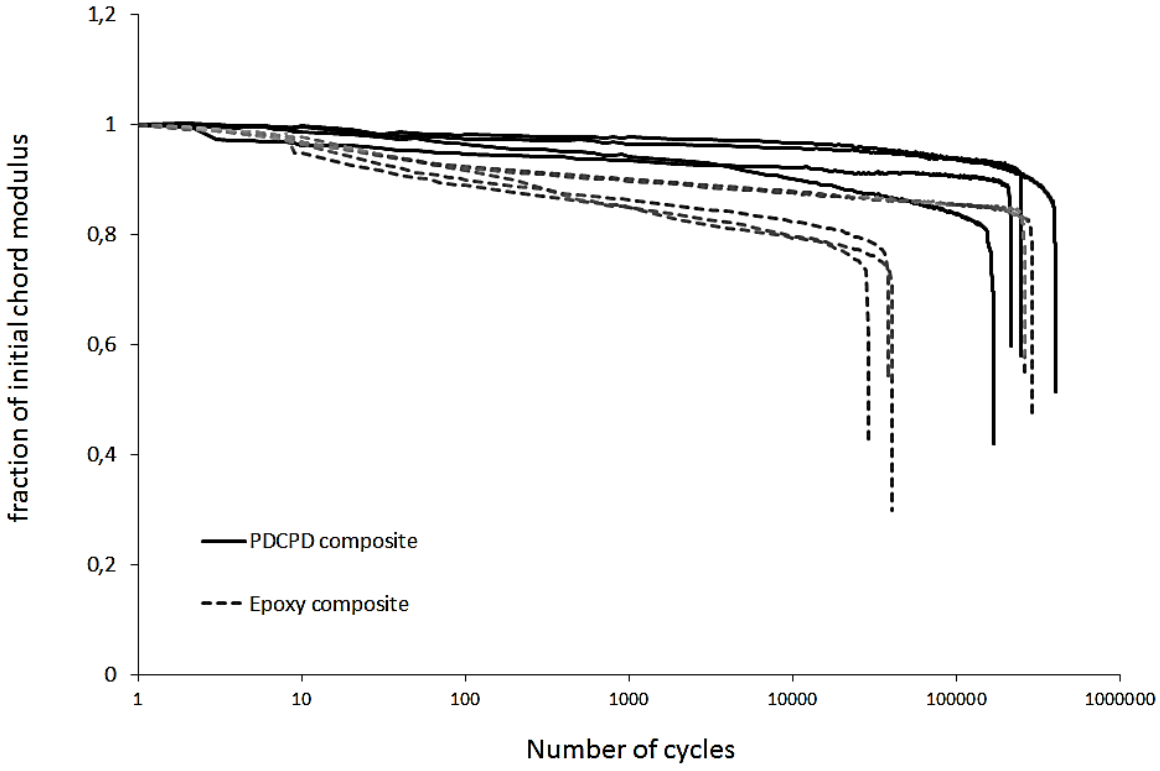
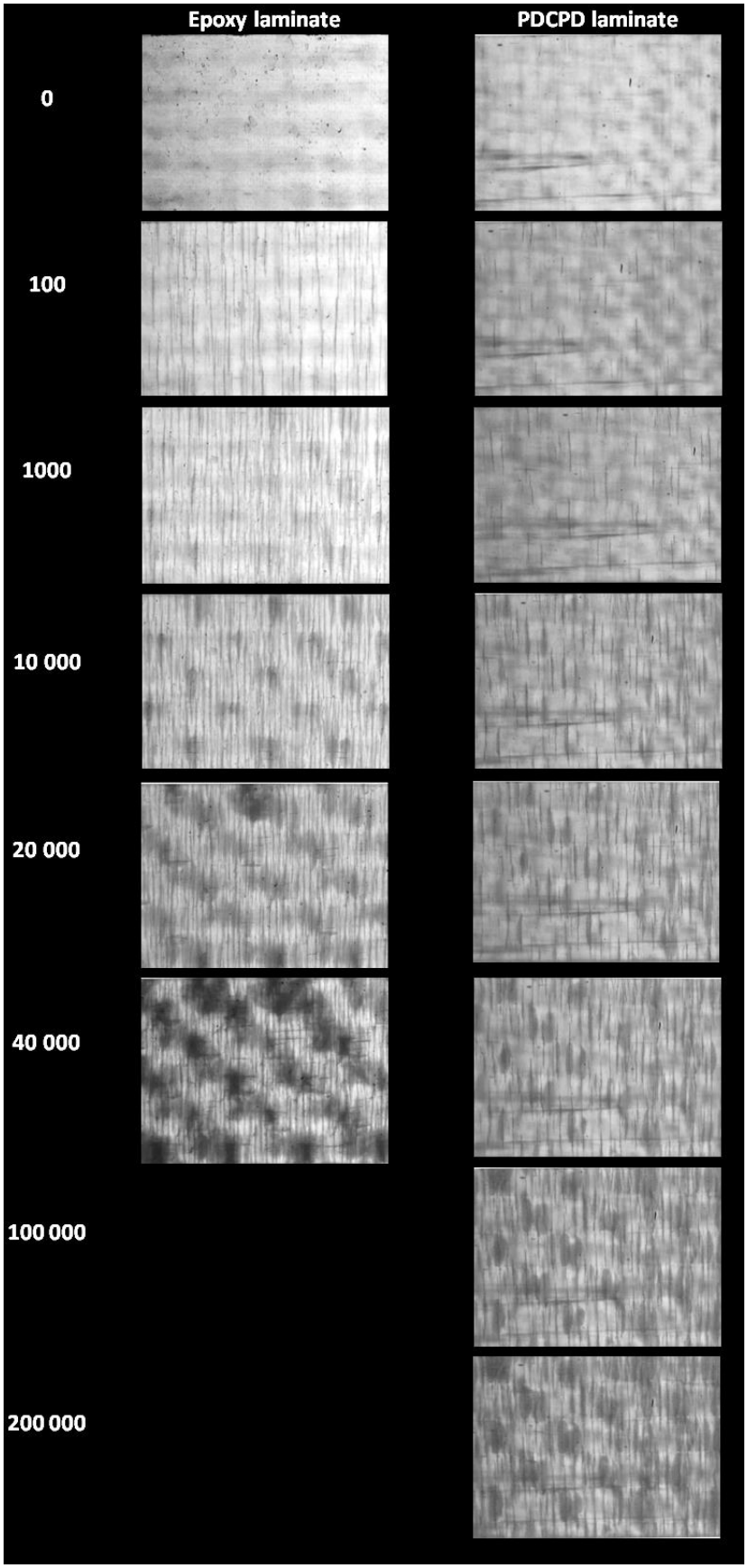


Figure 14: Evolution of the chord modulus of woven fabric composite samples tested in fatigue up to 150 MPa.



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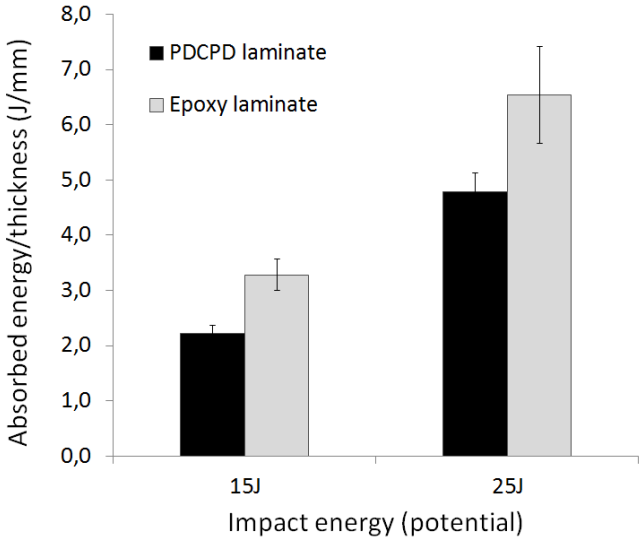

Figure 16: Absorbed energy per mm thickness for the two woven laminate materials, for an impact energy of 15 and 25 J.

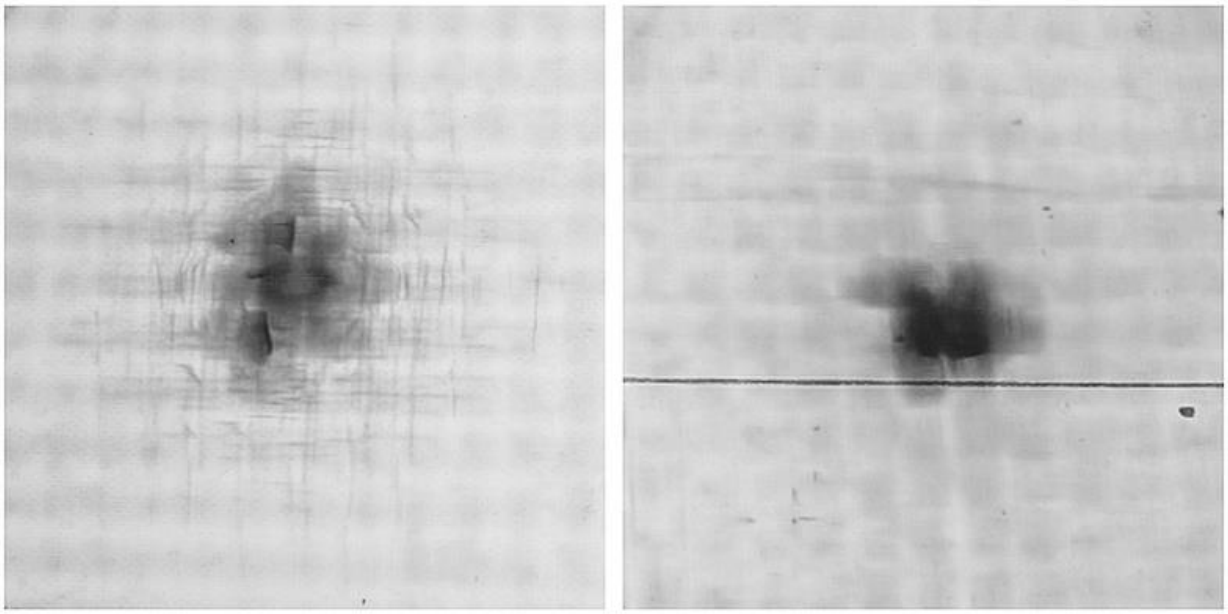

Figure 17: Transmitted light photograph of an epoxy laminate sample (left) and a PDCPD laminate sample (right), both impacted with an energy of 25 J. The scale for both pictures is the same.

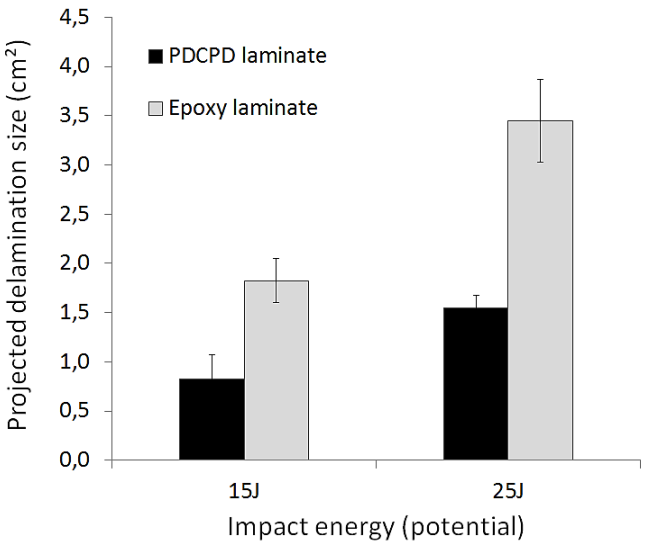

Figure 18: The projected delamination size for both materials and impact energies, as measured by ultrasonic c-scan.